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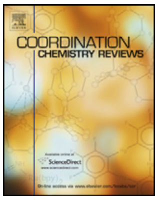

Review

Luminescent gold(I) complexes for chemosensing

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ABSTRACT

With the rich spectroscopic and luminescence properties associated with aurophilic Au···Au interactions, gold(I) complexes have provided an excellent platform for the design of luminescent chemosensors. This review concentrates on our recent exploration of luminescent gold(I) complexes in host–guest chemistry. Through the judicious design and choice of the functional receptor groups, specific chemosensors for cations and/or anions have been obtained. Utilization of sensing mechanisms based on the on–off switching of Au···Au interactions and photoinduced electron transfer (PET) has been successfully demonstrated. The two-coordinate nature of gold(I) complexes has also been utilized for the design of ditopic receptors through connecting both cation- and anion-binding sites within a single molecule.

1. Introduction

The exploration and development of gold(I) chemistry represent a fascinating and challenging area, and have attracted growing interest during the last two decades. Aurophilic Au···Au interactions have been one of the most intriguing topics in gold chemistry, and have been one of the reasons that has driven the rapid development of studies in gold in both the physical and chemical aspects. Short Au···Au contacts were often observed as a result of the relativistic effects and correlation effects [1–3], and Au···Au contacts of ca. 3.0 Å were estimated to have a bond energy of the order of 5–10 kcal mol^{-1} (21–42 kJ mol^{-1}) [1]. This energy is comparable to that of standard hydrogen bonds and thus provides extra stability to polynuclear gold(I) complexes. Numerous supramolecular structures based on gold(I) complexes have been designed and reported [4–32]; many of which show inter- or intramolecular Au···Au interactions. Recent reports have also shown that Au···Au interactions can direct the chiral assembly of a Au$_{16}$ macrocycle [4] and the supramolecular assembly of a Au$_{12}$ capsule [5], a Au$_{18}$ macrocycle [6] and a Au$_{36}$ crown [7].

Luminescence is another attractive property of gold(I) complexes [8–32]. The presence of the heavy gold center in these complexes will enhance the spin–orbit coupling of the system, which in turn will facilitate the access to the triplet excited state via intersystem crossing. Owing to the d^{10} electronic configuration of gold(I), d–d transitions cannot occur in gold(I) complexes, therefore studies in the luminescence properties of gold(I) complexes are advantageous. The first example on the luminescence proper-

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ties of the gold(I) complex, [Au(PPh_3)Cl], was reported by Dori and co-workers in 1970 [8]. Since then, luminescent gold(I) systems have been extensively studied by many research groups [9–32]. A number of mono-, di- and polynuclear gold(I) complexes with different types of ligands, such as phosphine [9–15], thiolate [16–20], chalcogenide [21–25], and alkynyl [26–30] have been investigated and exhibit interesting photophysical properties. The photochemistry and photophysics of gold(I) complexes have been reviewed very recently by Yam et al. [31,32].

It has become increasingly widely accepted that the Au···Au interaction is not only responsible for the wide range of structural diversity, but also can lead to the intriguing electronic absorption and luminescence properties. In general, an increase in the Au···Au interaction would lead to a shift of the emission to lower energy. In addition, the Au···Au interaction and the associated photophysical properties can be perturbed through different environmental stimuli, such as solvent, pH, pressure, mechanical properties and temperature. In 1997, Balch and co-workers reported the first example of solvent-stimulated luminescence (or solvoluminescence) of solid samples of trinuclear [$Au_3(MeN{=}COMe)_3$] [33]. Such solvoluminescence behavior was suggested to be related to the intermolecular aggregation present in the solid rather than to the discrete trinuclear monomers. An interesting phenomenon of vapochromism and VOC-induced luminescence behavior of [$Au_2\{S_2CN(C_5H_{11})_2\}_2$] was demonstrated and reported by Eisenberg and co-workers [34]. The X-ray study showed that the intermolecular gold–gold distances of the emissive solvated orange form and the non-emissive colorless form were 2.9617(7) Å and 8.135 Å, respectively. When the colorless non-emissive form was brought in contact with polar aprotic solvent vapors, luminescence could be restored. Heterometallic complexes of gold(I) have also been demonstrated to serve as vapochromic and vapoluminescent materials [35]. The vapochromic properties of a chain polymeric complex, $\{Tl[Au(C_6Cl_5)_2]\}_n$, in the presence of a series of VOCs were studied by Laguna and Fackler [35]. The color of the complex, as well as its emission energy upon photo-excitation, could be perturbed significantly upon exposure to a variety of organic vapors and reversed upon heating. These behaviors are associated with a weak interaction of the Tl(I) centers with the VOCs.

Luminescence tribochromism, which refers to a sustained change in the photoluminescence spectrum upon the initial application of a pressure, was demonstrated in a series of dinuclear gold(I) thiouracilate diphosphine complexes [36]. Recently, Ito et al. reported the mechanochromic luminescence behavior of [$(C_6F_5Au)_2(\mu$-1,4-diisocyanobenzene)] [37]. The photoluminescence of the solid, upon grinding, underwent a drastic color change and, upon exposure to solvents or their vapors, its original color was restored. Polymorphism of luminescent gold(I) complexes with or without close Au···Au contacts has also been observed. Two polymorphs of [$(C_6H_{11}NC)_2Au]PF_6$ have been isolated by Balch and co-workers [38]. [$(Cy_3P)Au(C{\equiv}CC_6H_4$-4-$NO_2)$] was also demonstrated to exhibit polymorphism in the solid state by Che and co-workers [39]. Gold(I) complexes can also form oligomer in solutions. Patterson, Fackler and co-workers systematically studied the effect of concentration, temperature and solvent on the oligomerization of $[Au(CN)_2]^-$ in solution, providing multiple evidences for the oligomerization of $[Au(CN)_2]^-$ via aurophilic interaction in solution and demonstrating the Au···Au excimer and exciplex photoluminescence behaviors [40,41].

In view of the need to search for host molecules that can selectively recognize specific guest molecules at a specific receptor site and produce measurable physical changes, attention has been focused on the molecular design of chemosensors that would involve optical signal transduction, particularly in luminescence signaling. In this review, we will mainly focus on the study of luminescent gold(I) complexes with various functional receptor groups, for cation and/or anion binding. Different approaches for the design of chemosensors based on the host–guest interactions of gold(I) complexes have been explored, including the utilization of the on–off switching of Au···Au interactions and photoinduced electron transfer (PET). In addition, design based on the two-coordinate nature of gold(I) has been explored for the construction of ditopic receptors.

2. Luminescent gold(I) complexes for cation sensing

Metal ions play an important role in the chemistry of many biological, environmental and physiological processes. Na^+, K^+, Mg^{2+}, and Ca^{2+} ions are involved in biological processes such as transmission of nerve impulses, muscle contraction, regulation of cell activity, and so on. Moreover, various metal ions such as Mg^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+}, are involved in metalloenzymes. Cu^{2+} ion is not only a commonly found metal pollutant but also an essential trace element in the biological system, particularly as one of the major sources of oxidative stress that is closely related to the neurodegenerative diseases. Hg^{2+}, Pb^{2+} and Cd^{2+} are toxic to organisms, and early detection in the environment is of particular concern. Because of their important role in a wide range of applications, much efforts have been devoted to the development of appropriate chemosensors for the detection of these metal ions.

2.1. Crown ether-containing gold(I) complexes

Macrocyclic crown ether receptors are one of most versatile classes of organic molecules for cation-binding since the first discovery by Pedersen in 1967 [42]. The complexation mechanism between metal cations and crown ether receptors is principally a Lewis acid–base phenomenon and a function of the size relationship between the ionic diameter of the cation and the diameter of the crown cavity. It has now been well established that polyoxa crown ethers are able to bind alkali and alkaline earth metal ions. The matching of the ionic diameter of the cation and the diameter of the crown cavity plays a major role in the complexation. Generally, when the ionic diameter of the cations is closely equal to the size of the crown cavity, a more stable complex can be formed, resulting in a greater binding affinity. For example, 12-crown-4 (1.20–1.50 Å) is selective for Li^+ ions (1.36 Å), 15-crown-5 (1.70–2.20 Å) for Na^+ ions (1.94 Å) and 18-crown-6 (2.60–3.20 Å) for K^+ ions (2.66 Å) [43]. The cation is assumed to be located in the cavity of the polyether ring by ion-dipole forces and this leads to the stoichiometry of 1:1 between the cation and the host compound. However, if the cation is too small, two cations will be located in one crown ether moiety and 2:1 complexes will be formed. On the contrary, when the cation appears to be too large to fit into the cavity, 1:2 “sandwich” complexes (e.g., K^+: 15-crown-5) will be formed.

Although the molecular recognition of crown ether compounds with organic fluorophoric units has been extensively studied based on fluorescence signaling, the utilization of transition metal complexes as luminescent metal ion sensors has been relatively less explored. It was in the recent years that there has been a growing attention on the utilization of metal complexes for such studies; however, most of them were focused on systems with metal-to-ligand charge-transfer (MLCT) excited states involving photoinduced electron transfer (PET) and Förster resonance energy transfer (FRET) mechanisms [44–48], while other excited states and mechanisms have been relatively much less explored. In view of the rich spectroscopic and luminescence properties exhibited

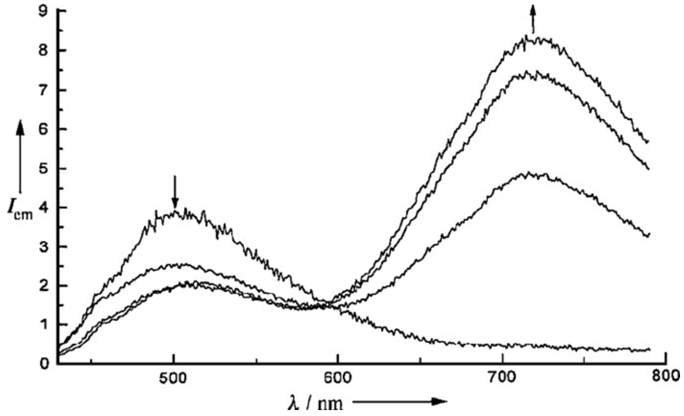
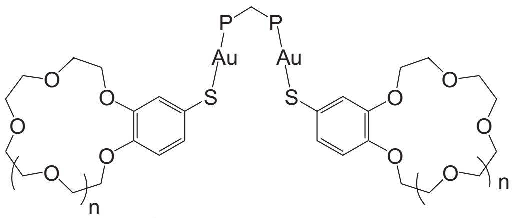


Fig. 1. Emission spectral changes of $[Au_2(dppm)(S\text{-}B15C5)_2]$ (**1b**) (1.7×10^{-3} M) upon addition of various concentrations of potassium ions in CH_2Cl_2–MeOH (1:1, v/v; 0.1 M $^nBu_4NPF_6$). Reproduced with permission from Ref. [49].

by gold(I) complexes and the interesting spectroscopic features associated with the unique Au···Au interactions, a number of gold(I) complexes containing crown ether pendants as chemosensing functionality have been designed and synthesized, and their ion-binding behavior studied. A new mechanism based on the utilization of the switching on and off of Au···Au interactions has also been developed in optical signal transduction for chemosensing.

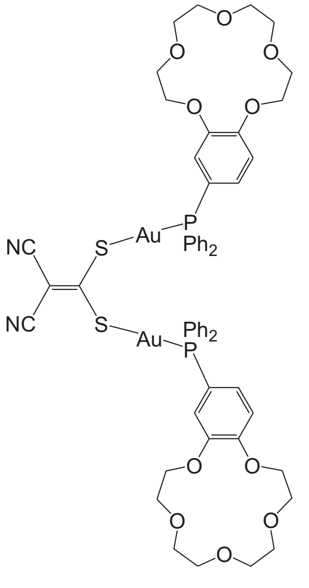
In 1998, we initiated a programme to explore the utilization of the switching on and off of Au···Au interactions in optical signal transduction for chemosensing. A series of dinuclear gold(I) complexes **1a**–**d** with bridging diphosphines and benzocrown-ether functionalized thiolate ligands, $[Au_2(P^\wedge P)(S\text{-}B15C5)_2]$ (S-B15C5 = 4′-mercaptobenzo-15-crown-5, P^P = dcpm, dppm) and $[Au_2(P^\wedge P)(S\text{-}B18C6)_2]$ (S-B18C6 = 4′-mercaptobenzo-18-crown-6, P^P = dcpm, dppm) have been reported [49,50]. All the dinuclear gold(I) complexes exhibited low-energy emissions at ca. 492–580 nm in dichloromethane solution at room temperature, which have been assigned as originating from states derived from a S → Au ligand-to-metal charge transfer (LMCT) origin. In addition, these complexes were demonstrated to be capable of sensing alkali metal ions, with specificity depending on the size of the crown ether pendants. Complexes **1a** and **b** with benzo-15-crown-5 moiety can act as luminescent ion probes for K^+. Upon addition of K^+, a drop in intensity at approximately 502 nm with the concomitant formation of a new long-lived, low-energy emission band at 720 nm was observed. Fig. 1 shows the luminescence response of **1b** towards K^+ ion binding. By changing the size of the crown ether pendants, complexes **1c** and **d** with benzo-18-crown-6 moiety can serve as luminescent sensors for Cs^+ ion. Similar low-energy emission bands were observed.



P^P = dcpm, n = 1 **1a**
P^P = dppm, n = 1 **1b**
P^P = dcpm, n = 2 **1c**
P^P = dppm, n = 2 **1d**

The lower energy emission bands are believed to originate from the thiolate-to-gold–gold ligand-to-metal-metal charge transfer (LMMCT) excited state. As shown in Fig. 2, when the alkali metal ions of appropriate size were encapsulated between two crown ether pendants in an intramolecular sandwiched fashion, i.e., K^+ ion between two benzo-15-crown-5 or Cs^+ ion between two benzo-18-crown-6 moieties, the two gold atoms would be brought into close proximity. Consequently, the intramolecular Au···Au interaction became “switched on” and the emission energy would be lowered according to the change of the emission nature from a ^{3}[RS → Au] LMCT to a ^{3}[RS → Au···Au] LMMCT origin.

As an extension of our research on dinuclear gold(I) complexes for cation sensing, a series of phosphine functionalized crown ether-containing gold(I) complexes with different bridging dithiolate ligands, $[Au_2(\mu\text{-}i\text{-mnt})(Ph_2P\text{–}B15C5)_2]$ (**2**) (i-mnt^{2-} = 1,1-dicyanoethylene-2,2-dithiolate, B15C5 = benzo-15-crown-5) and $[Au_2(\mu\text{-dtc})(Ph_2P\text{–}B15C5)_2](PF_6)$ (**3**) (dtc$^-$ = diethyldithiocarbamate), have been designed and synthesized [51]. The photophysical and ion-binding properties have been studied. The electronic absorption spectra of **2** and **3** are mainly dominated by high-energy absorptions at ca. 254–368 nm with low-energy tails extending all the way to ca. 400 nm. Well-defined isosbestic points in the UV–vis absorption spectra were observed upon addition of the metal cations, and these two complexes show preferential binding towards K^+ over Na^+. Evidence for the binding of metal cations to the dinuclear gold(I) complexes was also confirmed by the ESI-mass spectroscopy. An uncommon sandwiched structure of Na^+ between two crown moieties of complex **3** was found by X-ray crystal determination. The intramolecular Au···Au contact of 5.587(46) Å in the ion-free state of **2** was significantly longer than that of $[\mathbf{3}\cdot Na]^{2+}$ (3.0825(11) Å). However, such comparison may not be so reliable due to the difference in the bite angles between the two bridging ligands, i-mnt^{2-} and dtc$^-$. Nevertheless, these results provide an indirect proof demonstrating the idea that the metal ion-encapsulation process is capable of bringing the two gold(I) centers into close proximity to induce the formation of Au···Au interactions.



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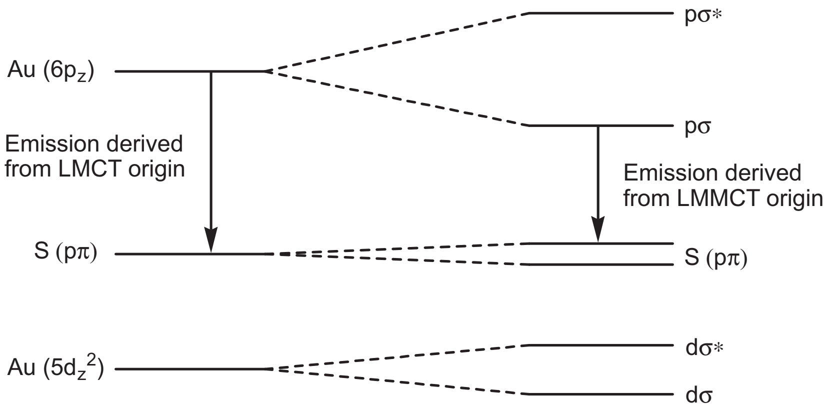


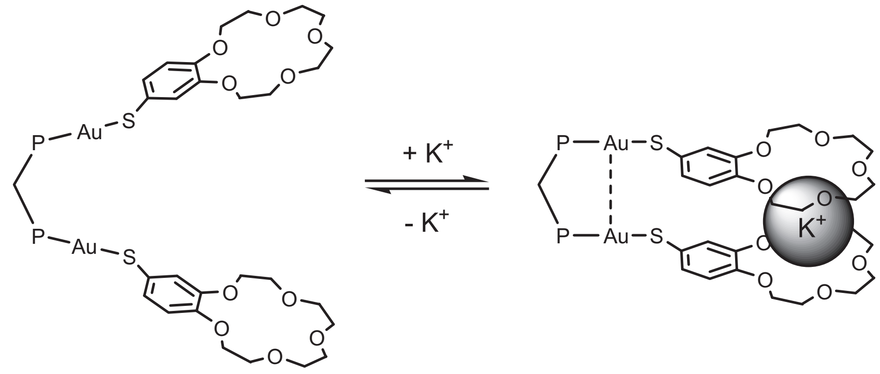
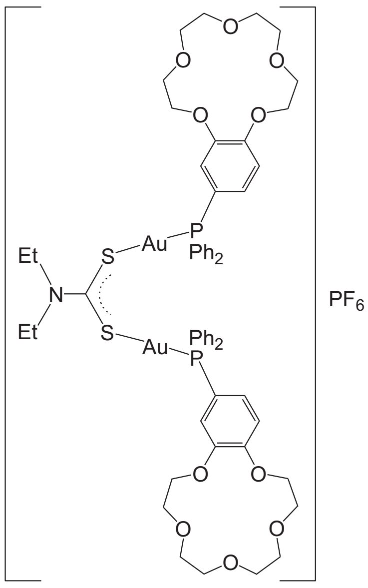
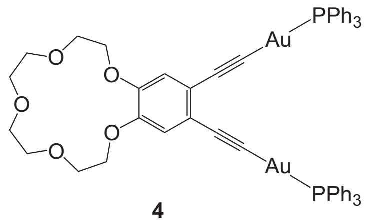


Fig. 2. Schematic representation of the orbital splittings expected with Au···Au interactions in dinuclear gold(I) thiolate complexes with bridging diphosphine ligands. Reproduced with permission from Ref. [50].



3

Apart from the exploration of mercapto- and phosphinobenzocrown-containing gold(I) complexes, ethynylcrown ether-containing di- and tetranuclear gold(I) phosphine complexes, [{(Ph$_3$P)AuC≡C}$_2$-4,5-B15C5] (**4**) and [{(Ph$_3$P)AuC≡C}$_4$-4,4′,5,5′-DB18C6] (**5**), have also been reported as luminescence chemosensors for alkali metal ions [52]. The alkynyl group, with its simple linear geometry, rigidity and conjugated π system which is usually involved in the luminescence origins, is a good candidate for the design of chemosensing systems. Introduction of gold(I) to the π-conjugated unsaturated alkynyl ligand has recently been shown to induce long-lived phosphorescence as a result of the heavy metal atom effect that enhances the spin–orbit coupling [28,53]. These complexes represent the few examples of disubstitution of ethynylgold(I) at the ortho positions of the benzene moiety. Complex **4** was synthesized by the reaction of (HC≡C)$_2$B15C5-4,5 with 2 equiv. of [Au(PPh$_3$)Cl] in the presence of an excess of triethylamine and a catalytic amount of CuI in THF. Complex **5** was prepared similarly and their structures have been established by X-ray crystallography. Intense absorptions at ca. 268–335 nm, with tails extending to ca. 400 nm for the dinuclear complex and ca. 500 nm for the tetranuclear complex were observed. The high-energy absorptions were assigned as IL transitions characteristic of triphenylphosphine, whereas the low-energy absorptions were assigned as [$\pi \rightarrow \pi^*$] IL transitions of the alkynyl ligands. Both complexes showed emission bands at 530–560 nm in dichloromethane and in the solid state at both room temperature and 77 K, which were suggested to arise from [$\sigma(\text{Au–P}) \rightarrow \pi^*(\text{C≡C})$] or metal-perturbed [$\pi \rightarrow \pi^*(\text{C≡C})$] IL excited states. The dinuclear gold(I) complex **4** with the benzo-15-crown-5 moiety had a binding affinity towards Na$^+$ ions, while the tetranuclear gold(I) complex **5** bearing the benzo-18-crown-6 showed a preferential binding towards K$^+$ ions. Observable UV-vis absorption spectral changes occur upon addition of Na$^+$ to **4** and K$^+$ to **5**. The log K_s values of **4** for Na$^+$ and **5** for K$^+$ ions are determined to be 3.2 and 5.1, respectively.



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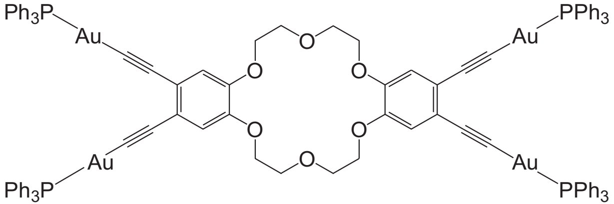
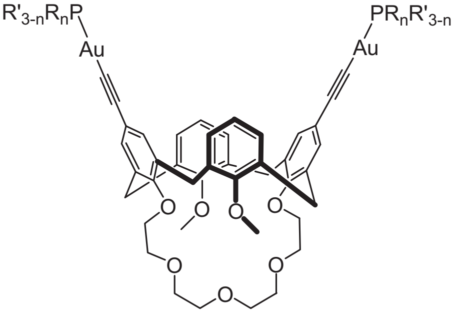


5

2.2. Calix[4]arene-based gold(I) complexes

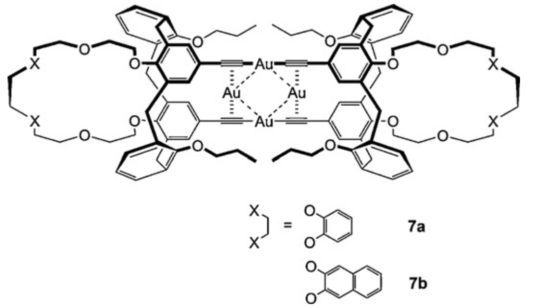
Calix[4]arenes are very useful building blocks and have been widely used in supramolecular assembly and chemosensing work [54,55]. The versatility of calixarenes as molecular platforms for the design and construction of elaborate supramolecular systems is mainly due to their unique molecular structures, simple one-pot preparations, easy chemical functionalization on the upper and lower rims, as well as their "tunable" molecular shapes and conformations. Various luminophores based on the calixarene framework for chemosensing work have been well documented and reviewed recently [56].While there have been much efforts to explore calixarene-based metal complexes [57–59] due to their potential application in catalysis, material science and chemosensing work [60], the study on gold(I) calixarene system is rare. Puddephatt and co-workers reported 1,3-dipropargyl calix[4]arenes by alkylation of the phenolic groups and their complexes with gold(I) and silver(I) [61]. Harvey and co-workers reported the mono- and tetrafunctionalization of the upper rim of calix[4]arene by isocyanide group and their corresponding gold(I) chloride complexes [62]. It was only recently that efforts have been made to explore the utilization of the gold(I) calixarene system as spectrochemical and luminescence ion probes.

A series of phosphinegold(I) alkynylcalix[4]crown-5 complexes, $[(R_nR'_{3-n}P)Au]_2L$ (**6a**–**e**) (n = 0–3; R = Ph, R′ = 2-C_6H_4Me, 4-C_6H_4Me; H_2L = 5,17-diethynyl-25,27-dimethoxy-calix[4]crown-5), has been designed and synthesized, and their photophysical and ion-binding properties studied [63,64]. All the complexes were fully characterized and their structures determined by X-ray crystallography. The intramolecular Au···Au separations of complexes **6a**–**e** were determined to be 8.567 Å, 6.696 Å, 6.729 Å, 8.764 Å and 8.870 Å, respectively, suggesting the absence of Au···Au interactions. These complexes showed high-energy [phosphine/ethynylcalixcrown] IL absorptions at 270–300 nm and low-energy absorptions at ca. 342 nm that were characteristic of the gold(I) alkynyl system. All the complexes showed an emission band at 578–585 nm in dichloromethane that was suggested to be derived from a triplet state of metal-perturbed IL or [$\sigma(\text{Au–P}) \rightarrow \pi^*(\text{phosphine})$] character. In general, the intraligand absorption band of the alkynylcalix[4]crown-5 exhibited a blue shift upon addition of alkali metal ions to a dichloromethane-methanol (1:1, v/v) solution of the complexes, with well-defined isosbestic points. In addition, all the complexes showed a higher selectivity for K^+ over Na^+. The K^+/Na^+ selectivities of complexes **6a**–**d** are 3×10^5, 1.8×10^2, 1.9×10^2 and 13, respectively. Similar findings on the preferential binding of K^+ ions over Na^+ for the cone conformation of the calix[4]crown-5 have been reported [65]. The binding properties of the complexes towards alkali metal ions (Na^+ and K^+) have been shown to be fine-tuned by a change in the different steric requirements of the auxiliary phosphine ligands. However, no significant changes in the luminescence properties of the complexes were observed upon addition of metal ions.



R = Ph, R' = *p*-Tol, n = 3 **6a**
R = Ph, R' = *p*-Tol, n = 2 **6b**
R = Ph, R' = *p*-Tol, n = 1 **6c**
R = Ph, R' = *p*-Tol, n = 0 **6d**
R = Ph, R' = *o*-Tol, n = 0 **6e**

In addition, discrete phosphine-free tetranuclear gold(I) alkynylcalixcrown complexes **7a** and **b** were also synthesized. Interestingly, both σ- and π-coordinated gold(I) centers were present in the system. Short intramolecular Au···Au contacts of 3.1344(8) and 3.2048(8) Å were observed, indicative of the presence of strong Au···Au interactions [66]. Unlike most other gold(I) alkynyl systems where the absence of ancillary ligands such as phosphines would lead to intractable polymeric or oligomeric solids that usually prevent them from further study and development [30,67], formation of insoluble polymeric gold(I) alkynyls was circumvented by the conformationally controlled and sterically protected calixcrown moieties. The complexes were highly emissive, with the emissions at ca. 587 nm and luminescence quantum yields of ca. 0.2 in chloroform at room temperature. Such emission was assigned to be derived from triplet states of metal-cluster-centered (ds/dp) character that were modified by Au···Au interactions, with some mixing of metal-perturbed intraligand character.



7a

7b

Besides the introduction of the gold(I) center onto the upper rim of calix[4]arene, functionalization of the lower rim has also been reported. Introduction of luminophore at the lower rim of calix[4]arene gives rise to less rigid structures, providing a high possibility to switch the luminescence through the conformation change upon the binding of guest species. Very recently, the design, synthesis and characterization of calixarene-based bis-alkynyl-bridged Au(I) isonitrile complexes with different crown ether pendants, [calix[4]arene-$(OCH_2CONH–C_6H_4C{\equiv}C)_2\{Au(CNR)\}_2$] (R = benzo-15-crown-5 (**8a**); R = benzo-18-crown-6 (**8b**)), were reported [68]. Introduction of the alkynyl and isocyanobenzocrown ligands to the gold(I) center has led to robust and sterically undemanding gold(I) complexes with stable Au–C bonds, which would be advantageous for ion-binding studies. Introduction of crown ether of different sizes has also led to selective binding towards various metal cations.

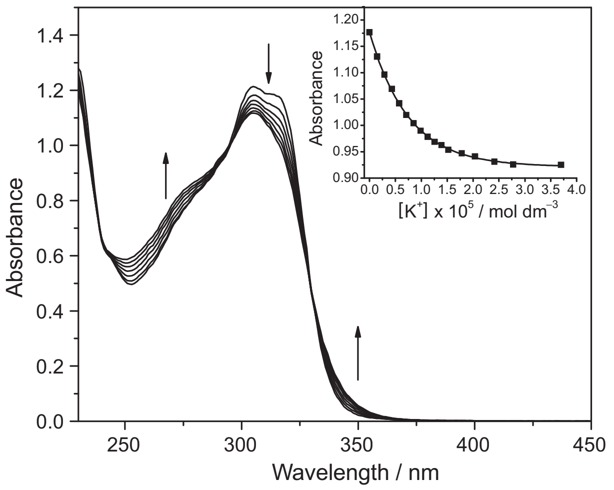


Fig. 3. Electronic absorption spectral traces of **8a** (1.45×10^{-5} M) in CH_2Cl_2–MeCN (1:1, v/v, 0.1 M $^nBu_4NPF_6$) upon addition of KPF_6 at 298 K. Inset: Plot of absorbance at 320 nm as a function of K^+ concentration and its theoretical fit for the 1:1 binding of complex **8a** with K^+. Reproduced with permission from Ref. [68].

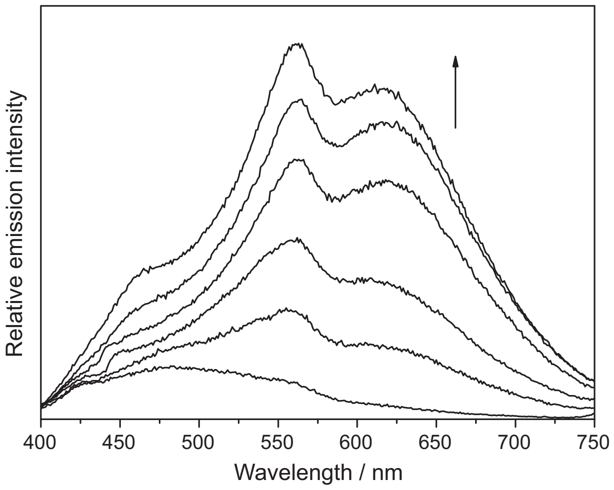
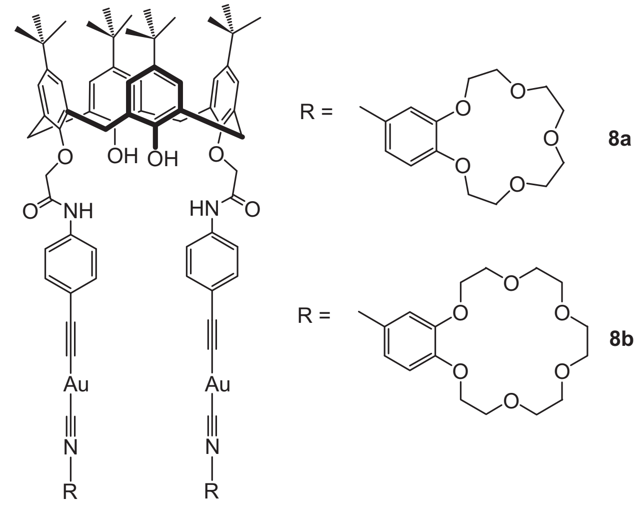


Fig. 4. Emission spectral changes of **8a** (6.6×10^{-5} M) upon addition of various concentrations of KPF_6 in CH_2Cl_2–MeCN (1:1, v/v; 0.1 M $^nBu_4NPF_6$). Excitation wavelength at 375 nm. Reproduced with permission from Ref. [68].



Complexes **8a** and **b** showed high-energy absorption bands at ca. 276–292 nm and lower-energy absorption bands at ca. 304–316 nm in CH_2Cl_2 solution. The high-energy absorption bands were assigned to the $\pi \rightarrow \pi^*$ intraligand transitions of the coordinated phenylalkynyl and the aryl isocyanide units, while the lower-energy absorption bands were attributed to arise from the ligand-to-ligand charge transfer (LLCT) transition. Excitation of the complexes in CH_2Cl_2 at 298 K gave emission bands centered at ca. 448–478 nm, which was assigned to states arising from a metal-perturbed intraligand $\pi \rightarrow \pi^*$ (C≡C) origin, with some mixing of an alkynyl-to-aryl isocyanide LLCT character.

The binding properties of these complexes with various metal ions have been studied using UV-vis, emission, ^1H NMR spectroscopy, and ESI-MS. The UV–vis absorption and emission responses of **8a** towards K^+ showed that Au···Au interactions were switched on upon the binding of K^+ in a sandwiched mode by the two benzo-15-crown-5 moieties. Figs. 3 and 4 show the UV–vis and emission spectral changes of complex **8a** upon addition of K^+ ions. The growth of a low-energy shoulder at 350 nm was observed, with the concomitant decrease of the absorption band at ca. 310 nm. The emission changes were found to be more pronounced, and a new low-energy band at ca. 600 nm was formed. The low-energy emission at 600 nm and the low-energy UV–vis absorption shoulder at 350 nm were attributed to result from the switching on of the Au···Au interaction upon the binding of the K^+ ion in a sandwiched binding mode, which gave rise to a reduced HOMO–LUMO energy gap. Due to the small size of Na^+ which would only bind to the cavity of the benzo-15-crown-5, no such lower energy band related to the switching on of the Au···Au interaction could be observed. The binding constants ($\log K_s$) of **8a** for K^+ and Na^+ were determined to be 5.80 ± 0.10 and 4.00 ± 0.01, respectively. The effect of crown size on the specificity of the metal ion-binding has also been investigated. Complex **8b** with benzo-18-crown-6 pendants showed selective binding towards Cs^+ and similar UV–vis absorption and emission changes were observed.

More structural information on the binding event was obtained from the ^1H NMR titration experiments and DFT calculation. The intramolecular hydrogen bonding interactions between the amide and the OH groups were weakened or destroyed due to the formation of a rigid sandwiched structure upon the binding of K^+ ion to **8a**. Fig. 5 shows the optimized geometries of **8a** and its K^+ ion-bound sandwiched adduct. A short Au···Au contact (3.178 Å) and a parallel-displaced configuration between the aryl rings of the two benzocrown moieties with a centroid–centroid distance of 3.648 Å were found in the K^+ ion-bound adduct, further supporting the presence of the Au···Au and π–π interactions in the sandwiched ion-bound mode.

2.3. *Gold(I) complexes with alkynyl moieties as binding site*

Alkynyl ligands can serve as π-donor ligands to bind different metal centers, resulting in the tuning of the luminescence behavior. The first report on the X-ray crystal structural characterization of η^2-alkynyl coordinated complexes dated back to 1974, when Abu Salah reported dimeric complexes that were formed by the π-coordination of iron alkynyls to halide-bridged copper centers [69]. Later on, the same group reported a series of polyheteronuclear coinage metal alkynyl complexes [70–74], demonstrating the presence and importance of both σ- and π-coordination modes in the metal alkynyl systems. The recent reports on luminescent systems of metal alkynyls such as $[\{\eta^2\text{-Re(bpy)(CO)}_3(C{\equiv}CPh)\}_2M]X$, $[Pt_2Cu_4(C{\equiv}CPh)_8]_2$ and $[Pt_2(dppm)_2(C{\equiv}CPh)_4\{M(MeCN)\}_2]X_2$ (M = Cu, Ag; X = PF_6, OTf) demonstrated that luminescence properties could be tuned through the perturbation of the electron richness of the alkynyl ligands via π-coordination to different metal centers [75–78].

Based on these concepts, attempts to make use of the gold(I) alkynyl complexes as π-donor metalloligands to coordinate to metal centers have been reported. The luminescence behavior of

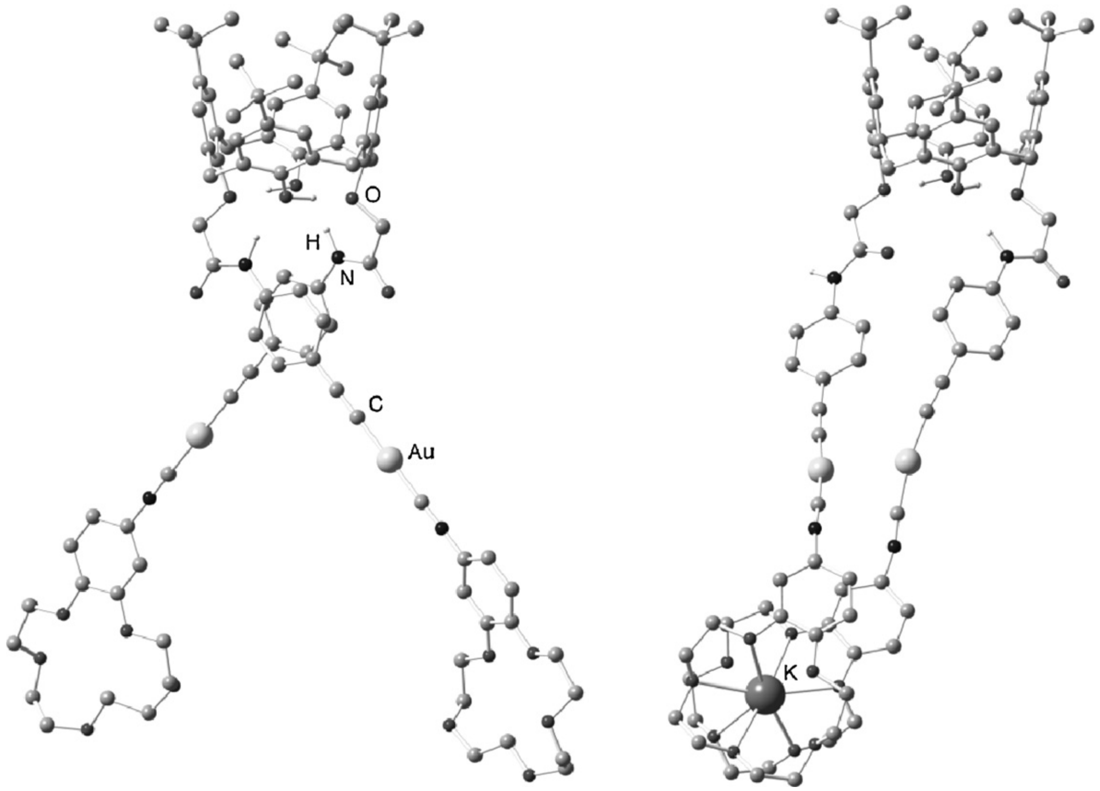


Fig. 5. The optimized geometries of **8a** (left) and its K$^+$ ion-bound sandwiched adduct (right). Hydrogen atoms except those on the amide and phenolic groups are omitted for clarity. Reproduced with permission from Ref. [68].

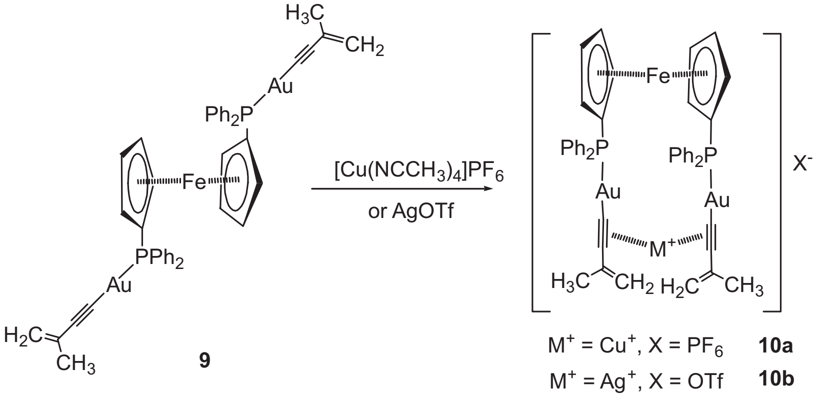


Fig. 6. Schematic binding mode of alkynyl π-bond donor to metal ion in phosphine gold(I) alkynyl complex. Reproduced with permission from Ref. [79].

a dinuclear gold(I) alkynyl complex with a bridging dppf ligand, $[(dppf)Au_2\{C{\equiv}CC(Me){=}CH_2)_2]$ (**9**), was switched on upon copper(I) or silver(I) encapsulation via π-coordination of the alkynyl moieties (Fig. 6) [79]. Complex **9** was non-emissive in the solid state, due to the efficient quenching of the ferrocenyl moiety. When Cu$^+$ or Ag$^+$ was encapsulated, the solid samples of complex **10a** and **b** showed low-energy emissions at ca. 583 and 565 nm, respectively. Such low-energy emissions were ascribed to be derived from states of a LMCT parentage mixed with a metal-centered $nd^9(n+1)s^1$ state, with some $\pi \rightarrow \pi^*$ IL character. The idea was further exemplified by using $[(P^\wedge P)Au_2(C{\equiv}CPh)_2]$ ($P^\wedge P$ = 4,6-bis(diphenylphosphino)dibenzofuran) as the bridging ligand. A hexanuclear dimeric Au$_4$Cu$_2$ complex, $[\{(P^\wedge P)Au_2(C{\equiv}CPh)_2\}_2Cu_2]$, could be isolated after the addition of copper(I) has been reported [80]. Close Cu···Au contacts of 2.8524(16) Å were observed, while no close Au···Au contacts were found.

An interesting macrocyclic azobenzene-containing tetranuclear gold(I) alkynyl phosphine complex, $[(dppm)Au_2(C{\equiv}CC_6H_4N{=}NC_6H_4C{\equiv}C)_2Au_2(dppm)]$ exhibits logic gate switching behavior [81]. The complex exhibited a $[\pi \rightarrow \pi^*(azo)]$ IL absorption band at 380–390 nm and a $[n \rightarrow \pi^*(azo)]$ IL absorption tail at 500 nm in dichloromethane solution, and the complex underwent photoisomerization. The *trans–trans* to *trans–cis* photoisomerization process of the azo moieties could be induced and reversed upon irradiation at different wavelengths. In addition, this photoswitching process could be modulated through the coordination and decoordination of silver(I) to the alkynyl groups in the tetranuclear macrocycle. As shown in Fig. 7, π-coordination of Ag$^+$ led to the conformational change of the macrocyclic gold(I) complex, which inhibited the photoisomerization process of the azo moieties. In contrast, addition of $^nBu_4NCl$ to the Ag$^+$-bound complex resulted in the

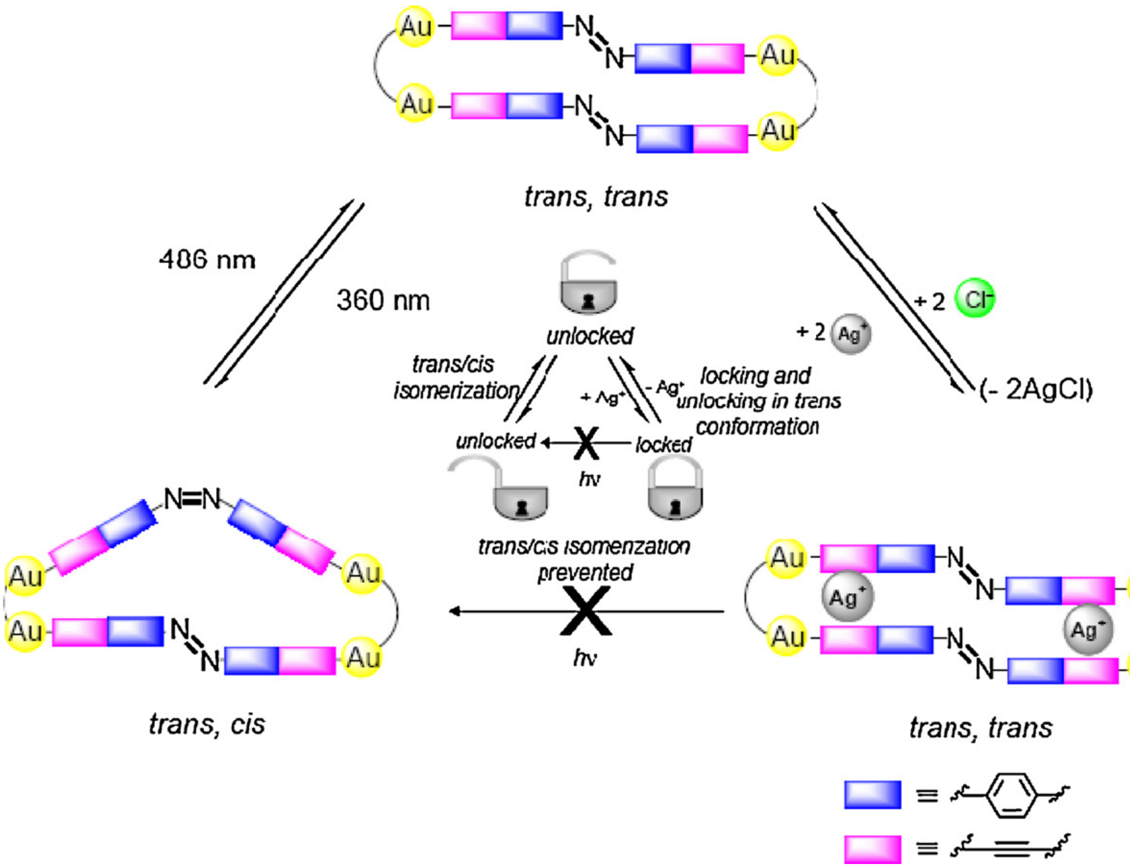


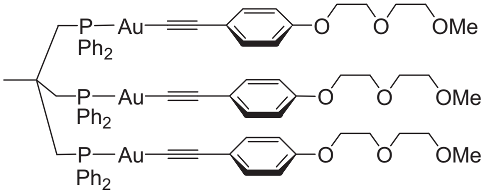
Fig. 7. Schematic diagram showing the “locking” and “unlocking” mechanism by the coordination and de-coordination of Ag^+ ions in $[(dppm)Au_2(C{\equiv}CC_6H_4N{=}NC_6H_4{-}C{\equiv}C)_2Au_2(dppm)]$. Reproduced with permission from Ref. [81].

abstraction of the Ag^+ ions, restoring the conformational flexibility and the photoisomerization process.

Recently, an interesting self-assembled supramolecular Au–Cu alkynyl heterometallic cluster, $[Au_3(PPh_2(C_6H_4)_2PPh_2)_3\{Au_6Cu_6(C{\equiv}CPh)_{12}\}](PF_6)_3$, was reported [82–84]. The cluster was formed by reacting the alkynylgold(I) diphosphine complex, $[C_6H_5C{\equiv}CAuPPh_2(C_6H_4)_2PPh_2Au{-}C{\equiv}CC_6H_5]$ with Cu(I). Variations in the length of the diphosphine ligand spacers resulted in the successful synthesis of a series of heterometallic complexes of the general formula $[\{Au_xCu_y(C{\equiv}CPh)_{2x}\}Au_3\{PPh_2(C_6H_4)_nPPh_2\}_3]^{3+(y-x)}$ $[n = 1, 2, 3; x = (n + 1)(n + 2)/2; y = n(n + 1)]$. All of the complexes exhibited strong room-temperature phosphorescence in solution with a maximum emission quantum yield of 0.92. The metal-centered triplet emission within the heterometallic alkynyl cluster was suggested to play a key role in the observed phosphorescence.

2.4. Tripodal gold(I) complex system with oligoether pendants

Apart from the macrocyclic receptors that are widely used in the design of cation-binding systems, the host–guest chemistry of chromophore-linked podand-based chemosensors has also been explored [85,86]. Although these acyclic ethers do not show strong binding affinity towards metal ions when compared to that of crown ethers, the conformation of these compounds could be drastically changed upon metal ion-binding. Therefore, noncyclic ether derivatives have received much attention. As an extension of the work in utilizing Au···Au interactions as signal transduction in the design of chemosensors, attempts have been made at increasing the extent of Au···Au interactions upon the binding of metal ions based on the motivation of the exploitation of podand-based receptors. A simple but novel trinuclear alkynylgold(I) complex **11** with three oligoether pendants has been designed and the photophysical and ion-binding properties studied [87].



11

The complex showed an electronic absorption spectrum similar to those of other alkynylgold(I) phosphine complexes, in which the high-energy absorption band at 288 nm was attributed to intraligand (IL) transitions characteristic of arylphosphine ligands, while the low-energy band at 324 nm was assigned to the $\pi \rightarrow \pi^*$ intraligand transition of the alkynyl ligand. The complex exhibited intense long-lived emission at 454 nm in dichloromethane at room temperature, which was attributed to the excited state arising from the $\sigma(Au{-}P) \rightarrow \pi^*(C{\equiv}C)$ or metal-perturbed intraligand $\pi \rightarrow \pi^*(C{\equiv}C)$ transition.

The cation-binding ability of complex **11** was studied, and it exhibited selective binding towards Mg^{2+} ions. The encapsulation of the Mg^{2+} ions in between the three intramolecular oligoether pendant units would force the three rigid and linear arylalkynylgold(I) units into close proximity, and as a result would lead to the turning on of the Au···Au interactions (Fig. 8). The switching on of Au···Au interactions would then lead to changes in the optical signal. Figs. 9 and 10 show the UV–vis absorption and emission

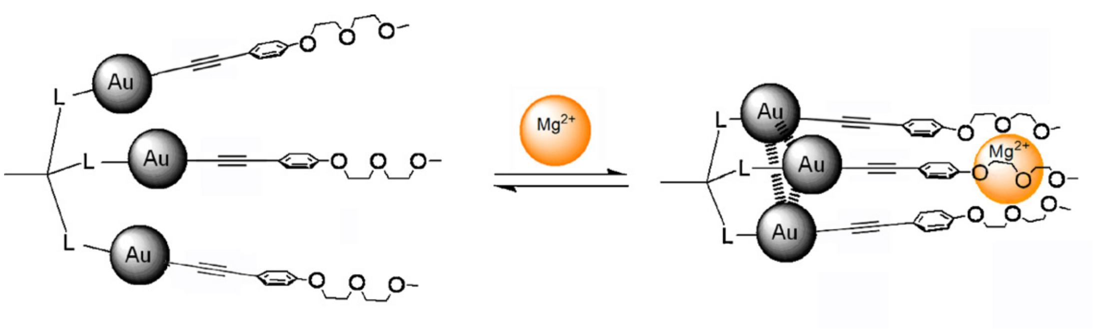


Fig. 8. Proposed binding mode for **11** and Mg^{2+}. Reproduced with permission from Ref. [87].

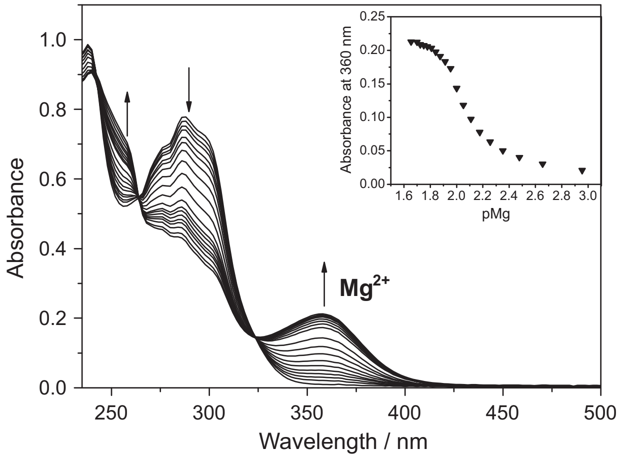


Fig. 9. UV–Vis spectral changes of complex **11** (1.1×10^{-5} M) in CH_2Cl_2–MeOH (1:1, v/v; 0.1 M $^nBu_4NPF_6$) upon addition of $Mg(ClO_4)_2$. Inset shows the absorbance changes at 360 nm of **11** upon titration of Mg^{2+}. Reproduced with permission from Ref. [87].

spectral changes of **11** in CH_2Cl_2–MeOH (1:1, v/v; 0.1 M $^nBu_4NPF_6$) solution upon addition of Mg^{2+}. The absorption band at ca. 290 nm showed a drop in intensity, with the growth of a new low-energy band at ca. 360 nm. In addition, a new low-energy emission band at ca. 675 nm was also observed. The low-energy emission band at 675 nm was attributed to originate from an excited state associated with the switching on of the Au···Au interactions upon the binding of Mg^{2+} that gave rise to a reduced HOMO–LUMO energy gap. For other metal ions (Ca^{2+}, Ba^{2+}, Li^+, Na^+, K^+), only Ca^{2+} showed a similar UV–vis change, but the change was to a much lesser extent, and the addition of other ions essentially showed no changes in the electronic absorption spectra. The selectivity for Mg^{2+} was due to the higher charge density and the smallest ion size, rendering the highest binding affinity to the oligoether pendants that brought the three Au atoms into close proximity.

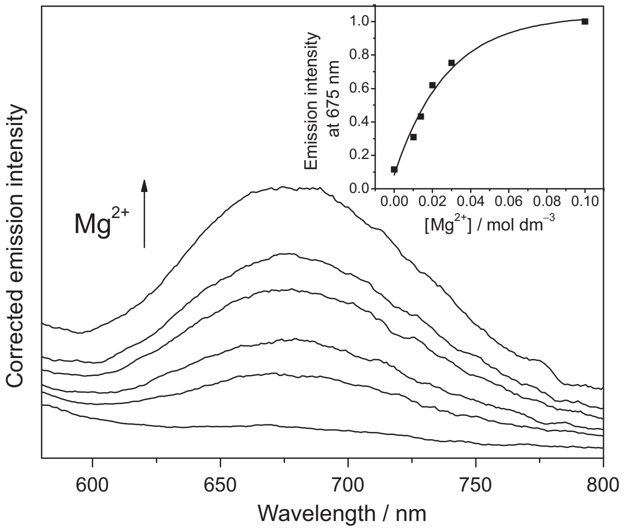
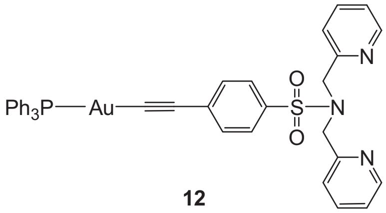


Fig. 10. Corrected emission spectral changes of complex **11** (1.0×10^{-4} M) in CH_2Cl_2–MeOH (1:1, v/v; 0.1 M $^nBu_4NPF_6$) upon addition of $Mg(ClO_4)_2$. Inset shows the plot of emission intensity at 675 nm as a function of Mg^{2+} concentration. Reproduced with permission from Ref. [87].

2.5. *Alkynylgold(I) complex system containing dipicolylamine receptors*

Dipicolylamine (DPA) is a well-known receptor which shows remarkable binding affinity towards transition metal ions and has been widely used in the design of sensors for molecular recognition [88–94]. Most of the previous studies focused on the attachment of the DPA unit to the organic fluorophores such as fluorescein [88–91] and Bodipy [92]. However, less exploration has been made on the use of luminescent inorganic/organometallic complexes [93]. Given the intriguing photophysical properties of the gold(I) alkynyl complexes, a novel luminescent alkynylgold(I) complex, $[(Ph_3P)Au(C{\equiv}CC_6H_4SO_2DPA)]$ (**12**) with the dipicolylamine receptor, has been designed and synthesized [94].



12

The X-ray crystal structure of complex **12** showed a P–Au–C angle of 174.9° that was close to linear geometry, typical of sp hybridization found in Au(I) alkynyl complexes. The shortest intermolecular Au···Au contact of 9.650 Å indicated the absence of Au···Au interactions. The complex showed an intense high-energy intraligand transition at 270–302 nm, with a tail extending to ca. 400 nm that was characteristic of the alkynylgold(I) complex. Excitation of complex **12** in CH_2Cl_2 gave a structured ligand-centered emission band at ca. 444 and 472 nm with vibrational progressional spacings of ca. 1336 cm^{-1}.

The ion-binding properties of the complex with various metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+} and Ni^{2+} have been studied by UV-vis, luminescence and NMR spectroscopy, and the complex was highly sensitive and selective towards Cu^{2+} ion. Addition of Cu^{2+} to a CH_2Cl_2–MeOH (1:1, v/v; 0.1 $^nBu_4NPF_6$) solution of **12** produced large spectral changes in both the UV–vis and emission spectra, as shown in Figs. 11 and 12. Upon addition of Cu^{2+}, a new low-energy absorp-

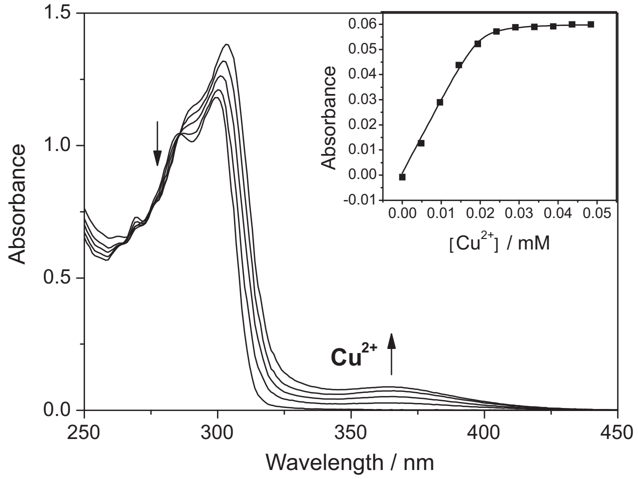


Fig. 11. UV–Vis spectral changes of complex **12** (2.0×10^{-5} M) in CH_2Cl_2–MeOH (1:1, v/v; 0.1 M $^nBu_4NPF_6$) upon addition of $Cu(ClO_4)_2$. Inset: A plot of absorbance at 366 nm as a function of Cu^{2+} concentration and its theoretical fit for the 1:1 binding of complex **12** with Cu^{2+}. Reproduced with permission from Ref. [94].

tion band at ca. 366 nm was formed, with a well-defined isosbestic point at 286 nm. The new band at ca. 366 nm was assigned as the ligand-to-metal charge transfer (LMCT) transition, arising from the transition of an electron from the lone pair of the amine group to the metal-centered orbital. In addition, significant emission quenching was observed as a result of the energy and/or electron transfer processes involving the d^9 electronic configuration of Cu^{2+}. The complex exhibited 1:1 binding towards Cu^{2+}, and the binding constants ($\log K_s$) were determined to be 6.2 ± 0.1 and 6.4 ± 0.1 by UV–vis and emission spectrophotometric methods respectively. The recognition event also shows complete reversibility, with the revival of the UV–vis and luminescence signals upon addition of EDTA.

The ^1H NMR titration study of **12** with Zn^{2+} showed that the proton resonances on the pyridine and phenyl rings were shifted downfield and became broader upon Zn^{2+} addition, which has been ascribed to the decrease in the electron density on the DPA unit and the conjugated phenyl ring. The binding constant $\log K_s$ for Zn^{2+} was determined to be 2.20 ± 0.05, which was much smaller than that for Cu^{2+}, suggesting the higher selectivity for Cu^{2+}.

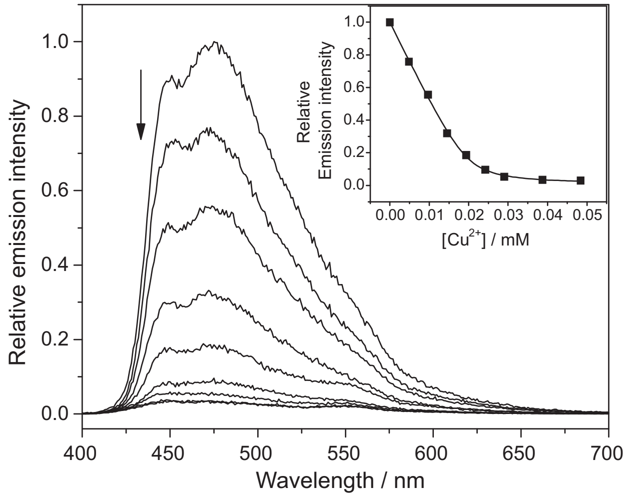
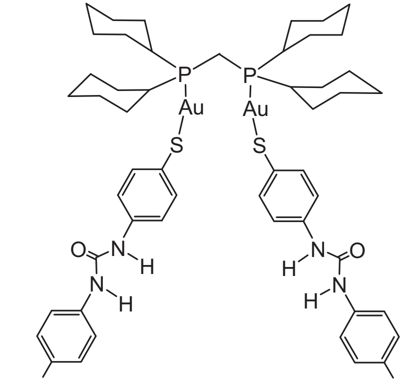


Fig. 12. Emission spectral traces of **12** (2.0×10^{-5} M) in CH_2Cl_2–MeOH (1:1, v/v; 0.1 M $^nBu_4NPF_6$) upon the treatment of $Cu(ClO_4)_2$. Excitation at the isosbestic wavelength of 286 nm. Inset: A plot of emission intensity at 475 nm as a function of Cu^{2+} concentration and its theoretical fit for the 1:1 binding of complex **12** with Cu^{2+}. Reproduced with permission from Ref. [94].

3. Urea-containing dinuclear gold(I) complexes for anion sensing

Research on anion binding and sensing has become a subject of increasing interest as the importance of the anions in biology, medicine, and the environment has been well realized [95–98]. Anion receptors based on transition metal complexes constitute a fast-growing field of research in this area, because of the diversity of their geometries, redox activities, photophysical properties, and their abilities to act as Lewis acids [99]. A wide range of metal complexes, such as those of iron(II), cobalt(II), ruthenium(II), rhenium(I), palladium(II), platinum(II), copper(II), and zinc (II), have been used in the design of anion sensors. However, examples of anion receptors based on gold(I) complexes are very rare. Recently, the design, synthesis and photophysical properties of a series of dinuclear phosphine gold(I) thiolate complexes **13**–**15** with bridging bis(dicyclohexylphosphino)methane (dcpm) ligand and various urea receptor pendants have been reported [100]. Through variation of the linker between the thiolate and the urea group and the electronic environment on the urea moiety, complexes **13**–**15** showed interesting photophysical and anion-binding properties.



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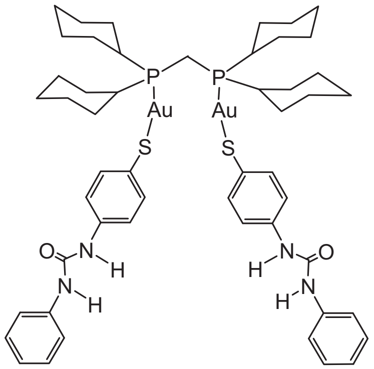

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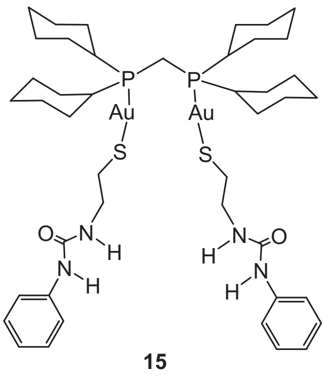

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The complexes showed intense high-energy absorption bands at ca. 240–300 nm in fluid solution. A low-energy tail extending to

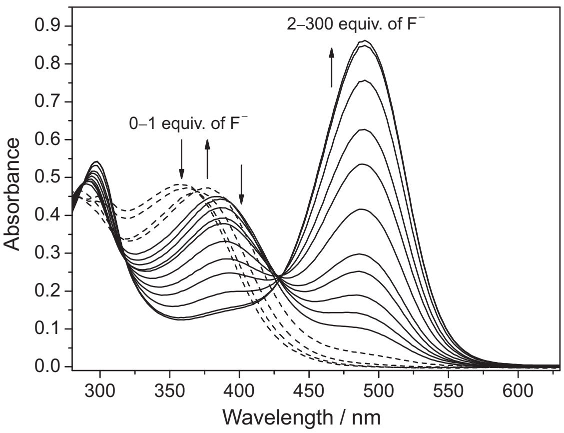


Fig. 13. UV–vis spectral changes of $[Au_2(dcpm)(SC_6H_4NHCONHC_6H_4NO_2\text{-}4)_2]$ (**13**) (1.17×10^{-5} M) in DMSO (0.1 M $^{n}Bu_4NPF_6$) upon addition of F^-. Reproduced with permission from Ref. [100].

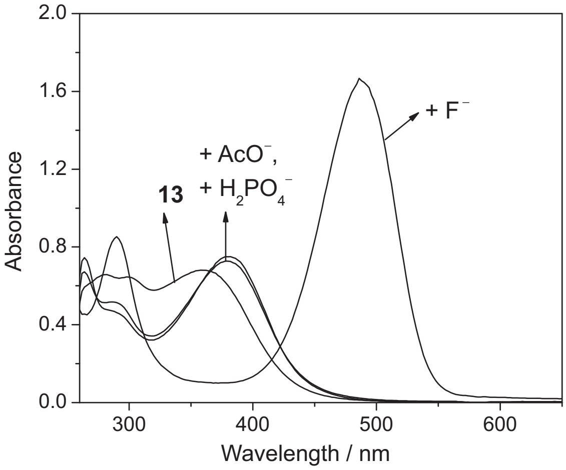


Fig. 14. UV–vis spectral changes of $[Au_2(dcpm)(SC_6H_4NHCONHC_6H_4NO_2\text{-}4)_2]$ (**13**) (2.0×10^{-5} M) in DMSO upon addition of 300 equiv. of F^-, AcO^- and $H_2PO_4^-$. Reproduced with permission from Ref. [100].

ca. 400 nm and a low-energy band at 310 nm were also observed for **14** and **15**, respectively. Complex **13** showed an additional intense low-energy absorption band at ca. 360 nm, which could be ascribed to the intramolecular charge transfer transition from the amide to the $-NO_2$ group. Excitation of complexes **14** and **15** in fluid solution at room temperature gave rise to intense LMCT/IL emissions at ca. 530–560 nm. However, complex **13** was non-emissive, probably due to the quenching effect of the NO_2 group. In the solid state and in the glass state at 77 K, complex **15** showed an intense low-energy orange–red luminescence at ca. 620 nm, which could be thought of as the overall result of the complementary aurophilic interaction and intramolecular urea–urea hydrogen bonding interaction.

The anion-binding studies have been investigated by NMR and UV–vis absorption spectroscopy. These urea-containing complexes formed hydrogen bonding interactions with anions in a 1:1 binding mode, and large downfield shifts of the urea NH proton signals could be observed in the ^1H NMR spectra. Obvious UV–vis spectral changes were also observed upon addition of basic anions, such as F^-, AcO^- and $H_2PO_4^-$, while the addition of Cl^-, Br^- and I^- led to negligible changes. The finding has been rationalized by the stronger binding affinity of the basic anions to the hydrogen-bond donor with acid character. The most pronounced UV–vis spectral changes, accompanied by a drastic color change from yellow to red, were observed upon addition of F^- to complex **13**, suggesting the potential use of **13** as a highly selective colorimetric probe for F^- ion sensing. Fig. 13 shows the electronic absorption spectral changes of **13** upon addition of F^- in DMSO solution (0.1 M $^{n}Bu_4NPF_6$). The interaction between **13** and F^- proceeded in two stages. In the first stage (0–1 equiv. of F^-), F^- would form hydrogen bonding interaction with complex **13**, with no noticeable color changes. Addition of more F^- (>1 equiv.) would lead to the deprotonation of the NH moieties, accompanied by a drastic color change from yellow to red. A new intense lower-energy absorption band at ca. 490 nm gradually appeared. These two processes were further confirmed in the ^1H NMR titration experiment. However, no obvious color changes could be observed in the presence of AcO^- or $H_2PO_4^-$, even in a large excess, as shown in Fig. 14. This suggested that **13** could serve as a selective colorimetric sensor for F^-. The spectral changes were similar to those observed upon the formation of hydrogen-bonding interaction between **13** and F^-.

Complexes **13** and **14** showed the same anion selectivity trend of $F^- > AcO^- > H_2PO_4^- > Cl^- \approx Br^- \approx I^-$, which was consistent with the trend in anion basicity. In addition, complex **13** exhibited higher binding affinity towards anions compared to that of complex **14**, due to the higher acidity of the urea moiety as a result of the introduction of the $-NO_2$ group. Complex **15**, with an ethylene linker between the thiolate and urea group, showed a lower anion-binding affinity than **13** and **14** as a result of the lower acidity of the urea protons than their aromatic counterparts. In addition, it was believed that the steric constraints imposed by the phenyl spacer would yield more well-defined binding pockets for analyte binding with **13** and **14**.

Unlike previous works on the dinuclear gold(I) complexes with crown ether pendants, which could be used as a luminescent probe for metal ions via the switching on and off of the Au···Au interactions [49,50], the emission response of these urea-containing dinuclear gold(I) systems to anion-binding was essentially negligible. This has been attributed to the fact that anions are usually larger in size than the corresponding isoelectronic cations and therefore have a lower charge density, which might not have the correct size and geometry to bring the two gold atoms into the appropriate distance (<3.4 Å) for an interaction to occur.

4. Mononuclear ditopic gold(I) complex containing both crown ether and urea receptors

Heteroditopic receptors incorporating both cation- and anion-binding sites within a single molecule have attracted much attention, because of their great potential applications such as in efficient extraction and as carrier transportation reagents for environmentally important ion-pair species [101–108]. The ditopic hosts are expected to exhibit allosteric and cooperative effects, where the binding of one ion would alter the association affinity of the counterion through electrostatic and conformational effects. The ion-pair recognition can also play an important role in controlling the geometry in supramolecular chemistry. Most of the studies on the heteroditopic hosts have focused on the organic molecules. However, ion-pair receptors based on metal complexes have been relatively much less explored [106,107]. In light of the two-coordinate nature of gold(I) complexes, the rich photophysical properties, as well as the good affinity of gold(I) to a variety of ligands, gold(I) complexes have been suggested to provide an ideal platform to construct ditopic receptors. A simple ditopic receptor based on the gold(I) phosphine thiolate complex $[(B15C5Ph_2P)Au(SC_6H_4NHCONHC_6H_5)]$ (**16**), together with its related crown-free analogue $[(Ph_3P)Au(SC_6H_4NHCONHC_6H_5)]$ (**17**), have been designed and isolated, and their photophysical properties studied [108]. Complex **16** featured both a benzo-15-crown-5 cation- binding unit in the auxiliary phosphine ligand and a urea-functionalized thiolate as an anion receptor moiety.

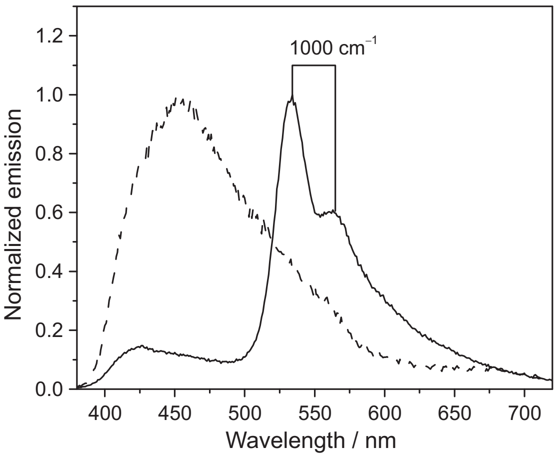
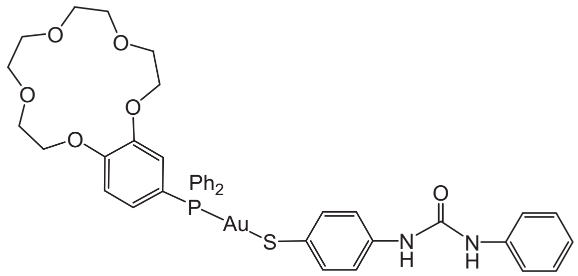
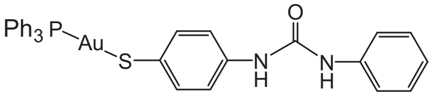


Fig. 15. Normalized emission spectra of **16** (---) and **17** (—) in dichloromethane at 298 K. Reproduced with permission from Ref. [106].



16



17

Complexes **16** and **17** show different emissions in CH_2Cl_2 solution, as shown in Fig. 15. The relatively weak low-energy emission of complex **16** has been attributed to the photoinduced electron transfer (PET) quenching effect of the electron-donating oligoether oxygen atoms on the crown ether moiety. In the solid state at 298 and 77 K, complex **16** exhibited a slightly higher LMCT/IL emission energy compared to that of **17**, which was attributed to the presence of the stronger electron-donating crown ether moiety on the phosphine ligand of complex **16**, rendering the gold(I) atom more electron-rich, and hence increases the thiolate-to-gold LMCT transition energy. The anion-binding studies in the absence and in the presence of Na^+ have been carried out using ^1H NMR spectroscopy. The results showed good 1:1 binding of **16** with anions, with a stability trend of $Cl^- > Br^- \gg I^-$. The binding constants K_s for **16** towards Cl^-, Br^-, and I^- were determined to be 599 ± 90, 109 ± 15, and $16 \pm 2\,M^{-1}$, respectively. In addition, for I^- with the largest size, a larger binding constant was observed in the presence of Na^+, suggesting a positive cooperativity effect. The results were consistent with the recent report suggesting that an anion with larger size would tend to give larger cation-induced affinity [103]. The ditopic receptor **16** also showed a good ability to solubilize NaCl and NaI salts in organic chloroform solution, as evidenced by the ^1H NMR and ESI-MS experiments. Crown-free complex **17** showed essentially negligible capability in such solid-liquid transport of NaCl, suggesting the ditopic composition is essential for the complexation of simple salt.

5. Concluding remarks

This review summarized selected recent efforts on the molecular design of luminescent gold(I) complexes with various functional receptor groups for cation- and/or anion-binding. Several approaches for the design of chemosensors based on the host–guest interactions of gold(I) complexes have been explored, including the utilization of the on-off switching of Au···Au interactions and photoinduced electron transfer (PET). In addition, the gold(I) metal center has been demonstrated to serve as the basic unit for assembly, and the two-coordinate nature of gold(I) complexes has been further utilized for the design of ditopic receptors.

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